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16. ABSTRACT

Kinetic expressions for the aqueous reactions of chlorine with phenanthrene (pH 3-10), fluorene (pH 3-5), and fluoranthene (pH 3-5) have been developed. At pH 3-5 the rate of reaction of each PAH studied could be related to the chlorine concentration ($-d[PAH]/dt = k_3[Cl_2]\cdot[PAH]$). Phenanthrene, also studied at high pH values (pH >8.8), followed a rate expression consistent with pseudo-first-order kinetics ($-d[phen]/dt = ([OCl^-]/(A + B[OCl^-]))[PAH]$). The overall rate expression that was developed for phenanthrene is suggested as a model for correlating the rates of reaction of chlorine with polynuclear aromatic compounds in water over the entire pH range (pH 3-10) that might reasonably be encountered during disinfection. The overall expression is

$$\frac{-d[phen]}{dt} = \left(\frac{[OCl^-] + C[HOCl]}{A + B[OCl^-] + D[HOCl] + E[Cl_2]} + k_3[Cl_2]\right)[phen]$$

The arene oxide (phenantherene 9,10-oxide) was the predominant phenanthrene product at pH >4 while phenanthrene-9,10-dione and 9-chlorophenanthrene were the major products at pH <4.

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JOURNAL ARTICLE

Chlorine "Disinfection" Chemistry of Aromatic Compounds. Polynuclear Aromatic Hydrocarbons: Rates, Products, and Mechanisms

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■ Kinetic expressions for the aqueous reactions of chlorine with phenanthrene (pH 3–10), fluorene (pH 3–5), and fluoranthene (pH 3–5) have been developed. At pH 3–5 the rate of reaction of each PAH studied could be related to the chlorine concentration ($-d[PAH]/dt = k_3[Cl_2]\cdot[PAH]$). Phenanthrene, also studied at high pH values (pH >8.8), followed a rate expression consistent with pseudo-first-order kinetics ($-d[phen]/dt = ([OCl^-]/(A + B[OCl^-]))[PAH]$). The overall rate expression that was developed for phenanthrene is suggested as a model for correlating the rates of reaction of chlorine with polynuclear aromatic compounds in water over the entire pH range (pH 3–10) that might reasonably be encountered during disinfection. This overall expression is

$$\frac{-d[phen]}{dt} = \left(\frac{[OCl^-] + C[HOCl]}{A + B[OCl^-] + D[HOCl] + E[Cl_2]} + k_3[Cl_2]\right)[phen]$$

The arene oxide (phenanthrene 9,10-oxide) was the predominant phenanthrene product at pH ≳4 while phenanthrene-9,10-dione and 9-chlorophenanthrene were the major products at pH ≲4.

Introduction

The use of chlorine for water renovation and disinfection has been questioned because of the reaction of active chlorine species with organic compounds present in water to form products that may be biologically harmful (*1*). Among the organic species known to be present during chlorination are the polynuclear aromatic hydrocarbons (PAH), a class of ubiquitous compounds that may be the precursors to at least a portion of the undesirable products (*2*, *3*).

Some of the products obtained upon aqueous chlorination of various PAH compounds have been reported by our laboratory (*4*, *5*) and others (*6*). However, the kinetics of chlorination of PAH in water have not been thoroughly investigated. In a study (*7*) with pyrene and benzo[*ghi*]-perylene, it was found that the reacting species were HOCl and, possibly, H_2OCl^+. Species that have been shown to be involved in the aqueous chlorination of other types of organic molecules included Cl_2 (*8*), HOCl (*9*), OCl^- (*10*), H_2OCl^+ (*11*), and/or Cl_2O (*9*, *11–13*), but not Cl^+ (*9*, *11*, *14*). In the present article we will describe a detailed study of the kinetics and product distributions of phenanthrene in the pH range 3–10 and fluorene and fluoranthene in the pH range 3–5.

The relevant pH-dependent chlorine–water equilibria are shown in eq 1 and 2. Although aqueous solutions of

$$Cl_2 + H_2O \underset{k_1'}{\overset{k_2}{\rightleftharpoons}} H^+ + Cl^- + HOCl \quad (1)$$

$$K_{Cl_2} = k_2/k_1 = 3.38 \times 10^{-4} \text{ (20 °C (25))}$$

$$HOCl \rightleftharpoons H^+ + OCl^- \quad (2)$$

$$K_{HOCl} = 2.62 \times 10^{-8} \text{ (20 °C (26))}$$

hypochlorous acid and hypochlorite only slowly decompose to chlorate and oxygen (*15–23*), it is known that hypochlorite is rapidly converted to the same products in the presence of ultraviolet light via the intermediates $O(^3P)$, Cl·, and O^- (*24*).

Experimental Section

Instruments and Apparatus. The GC–MS instrument was a Hewlett-Packard 5993B equipped with an Avondale B capillary inlet and modified GC–MS interface that allowed the entire effluent of the fused silica column (J & W Scientific, 15 m × 0.32 mm, DB-5) to be drawn into the ion source. The HPLC apparatus consisted of a Perkin-Elmer Series 3 pumping system, a 7126 Rheodyne injector, a Perkin-Elmer C-18 column (0.26 × 25 cm, P.N. 089-0716), maintained at 25 °C with a constant-temperature bath and circulator to ensure reproducible retention times (±0.03 min), a Waters Model 440 UV detector (254 nm), a Perkin-Elmer LC-75 UV detector (280 nm), and a Waters data module. The sample loops varied in size from 175 μL to 4.10 mL depending upon sensitivity requirements. The linear solvent program utilized was 5% acetonitrile in water to 100% acetonitrile in 10 min with a flow rate of 1.5 mL/min. NMR spectra were obtained on a Varian 360L instrument. Melting points were obtained on a Thomas-Hoover apparatus and are corrected.

Chemicals. Phenanthrene, fluorene, fluoranthene, 9-chlorophenanthrene, diphenic acid, phenanthrenequinone, and diphenic acid anhydride were obtained from the Aldrich Chemical Co. and further purified by recrystallization and/or sublimation as required. The chlorine was

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obtained from Mallinckrodt. The following salts were also obtained commercially: sodium perchlorate (G. Frederick Smith), potassium phosphate monobasic (Fisher Scientific), and sodium hydroxide (Baker analyzed). The water was obtained from a Milli-Q (Millipore Corp) system and boiled for 0.5 h before use.

Kinetics. A solution of the PAH (ca. 10^{-6} M) was prepared by allowing water containing appropriate amounts of sodium perchlorate, potassium dihydrogen phosphate, perchloric acid, and/or sodium hydroxide (for a final ionic strength of 0.01 M) to flow through a glass column containing glass beads coated with the PAH. This solution was monitored by HPLC for several hours or more prior to initiation of a reaction to ensure that the PAH concentration was constant and presumably no crystalline material was present.

An aqueous solution of chlorine was prepared just prior to the start of an experiment by bubbling chlorine gas into water. The pH of the solution was measured before and after the bubbling process. The chloride ion concentration was assumed to be equal to the difference in hydrogen ion concentration (25). Adjustment of the pH was accomplished with perchloric acid or sodium hydroxide solution.

A reaction was initiated by allowing 1.3 L of the PAH solution and 0.7 L of the chlorine solution to flow together in a Y-tube. The reaction solution was maintained in the dark at 20.0 °C in a constant-temperature bath. The pH and chlorine concentration [iodometric titration (27)] were monitored throughout the reaction. The concentration of the HOCl, OCl^-, and Cl_2 were calculated according to eq 1 and 2. The concentrations of PAH and products were monitored by HPLC. Aliquots of the reaction mixture were either quenched with sodium thiosulfate solution and retained for subsequent HPLC analysis or were injected directly where interferences were noted (e.g., phenanthrene 9,10-oxide reacts with thiosulfate to form an addition product). Standard curves for these analyses were prepared from authentic compounds. 9-Phenanthrenol and phenanthrene 9,10-oxide, which were found to coelute from the HPLC column, were quantitated by utilizing the peak areas obtained from each of the detectors (254 and 280 nm).

The presence of phosphate buffer in reactions at pH 6–8 did not appear to alter the rate from that obtained in reactions in which the ionic strength was maintained instead by sodium perchlorate. Reactions carried out with an oxygen or argon blanket also were unaffected.

Product Identification. Water (12 L) was treated with chlorine gas, and an appropriate amount of sodium hydroxide was added to achieve the desired pH. A solution of the PAH in acetonitrile was added to initiate a reaction, which was monitored by HPLC. No change in product distribution was observed with changes in acetonitrile concentration. Upon completion of the reaction, 2.5–3 equiv. (based on the total chlorine concentration) of dimethyl sulfoxide or sodium thiosulfate were added. In some cases, the reactant solution was acidified with sulfuric acid in order to suppress ionization of acidic products. The solution was then forced through two 7 × 50 mm stainless steel adsorption columns connected in series. The first column contained C-18 Porasil (37–75 μm, Waters Assoc.) and the second contained XAD-2 (100 μm, Rohm and Haas). Reaction products that were adsorbed were later removed by elution of the column train with acetonitrile and then with methylene chloride. Some separation of these products was observed during the elution process. The various fractions collected were then checked for trogen stream prior to analysis by gas chromatography–mass spectrometry (GC–MS). Portions of fractions suspected of containing acidic compounds were treated with diazomethane.

Authentic Standards. The following compounds were prepared according to literature methods: phenanthrene 9,10-oxide (*28*), *trans*-9,10-dihydro-9,10-dihydroxyphenanthrene (*29*), 2-chlorofluorene (*30*), and 3-chlorofluoranthene (*31*).

9-Phenanthrenol was prepared by the rearrangement of phenanthrene 9,10-oxide with base. Diisopropylamine (0.47 g, 0.0047 mmol) and *n*-butyllithium (3.23 mL of 1.6 M solution in hexane, 0.0052 mol) were combined in tetrahydrofuran (THF) at −78 °C under N_2. A slurry of phenanthrene 9,10-oxide (0.911 g in THF, 0.10047 mol) was added by syringe, and the mixture was then allowed to warm slowly overnight. Sulfuric acid (1 N) was added, the mixture was twice extracted with benzene, and the combined extracts were dried with magnesium sulfate and evaporated in a rotary evaporator at 30 °C. Tan crystals (0.844 g, 92%) resulted, mp 144–147 °C. Recrystallization from benzene gave tan crystals, mp 149–151 °C (lit mp 151–152 °C)(*32*)). IR (KBr) showed the absence of phenanthrene-9,10-dione. This phenol undergoes rapid autoxidation to this quinone (*33*) at such a rate as to preclude the preparation of pure solutions. The generation of an HPLC standard curve required correction for the amount of quinone present.

9,10-Dichlorophenanthrene was prepared by the chlorination of phenanthrene. Methylene chloride (100 mL) and commercial bleach (100 mL) were combined in a closed container, and the aqueous layer was adjusted to pH 4 with phosphoric acid (*28*). The total chlorine content of the two layers was determined by iodometric titration to be 0.03 M. Phenanthrene (0.85 g, 0.0048 mol) was added and the mixture stirred at room temperature for 5 h. The organic layer was then removed, washed with water, and saturated with sodium thiosulfate solution, dried over magnesium sulfate, and evaporated to yield a yellow solid (80%). Recrystallization from methanol and again from acetonitrile gave tan crystals: mp 157.5–159 °C (lit. mp 158–160 °C) (*34*)); NMR ($CDCl_3$) δ 7.6–8.1 (m, 4 H), 8.4–9.0 (m, 4 H).

Results and Discussion

Pseudo-first-order kinetics ([total of all chlorine species] ≫ [PAH]) were observed for all reactions in the pH range studied (pH 3–10; eq 3,4; e.g., pH 4.04; Figure 1 (*4*, *5*)).

$$-d[PAH]/dt = k_{obsd}[PAH] \quad (3)$$

$$-\ln [PAH]_{t=t} = k_{obsd}t - \ln [PAH]_{t=0} \quad (4)$$

Low pH. The observed rate constants, k_{obsd}, for reactions at pH ≲4 were found to be directly proportional to the Cl_2 concentration calculated by consideration of the equilibrium shown in eq 1 (Figure 2 and 3). Second-order rate constants, k_3, were determined by least-squares analysis of the k_{obsd} vs. $[Cl_2]$ data (k_3, M^{-1} s^{-1}; fluorene, (3.66 ± 0.03) × 10^2; phenanthrene, (6.32 ± 0.12) × 10^3; fluoranthene, (6.74 ± 0.36) × 10^2)). Thus, predicted pseudo-first-order rate constants for low pH reactions, $k_{obsd}^{Cl_2}$ can be calculated by eq 5.

$$k_{obsd}^{Cl_2} = k_3[Cl_2] = k_3\left(\frac{\gamma^2[H^+][Cl^-][HOCl]}{K_{Cl_2}}\right) \quad (5)$$

A process consistent with these results is shown in eq

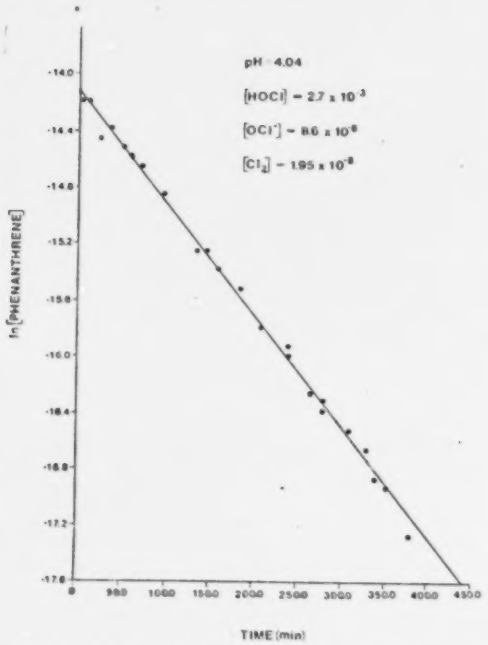


Figure 1. Pseudo-first-order plot for a typical phenanthrene reaction at low pH.

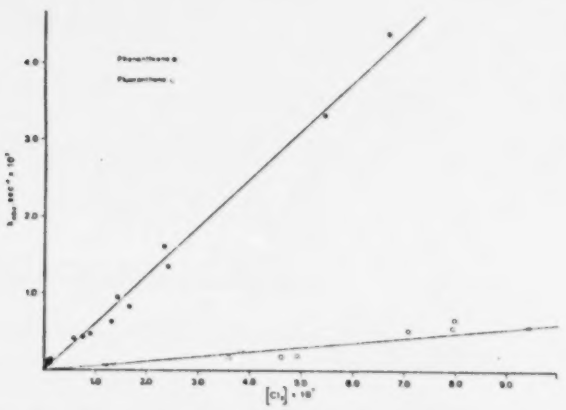


Figure 2. Dependence of k_{obsd} upon $[Cl_2]$ at low pH for phenanthrene and fluoranthene.

6 and 7 along with the corresponding rate equations, eq 8 and 9.

$$HOCl + H^+ + Cl^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Cl_2 + H_2O \quad (6)$$

$$Cl_2 + PAH \xrightarrow{k_3} \text{products} \quad (7)$$

$$-d[PAH]/dt = k_3[Cl_2][PAH] \quad (8)$$

$$d[Cl_2]/dt = k_1\gamma^2[HOCl][H^+][Cl^-] - k_2[Cl_2] - k_3[Cl_2][PAH] \quad (9)$$

Assuming $d[Cl_2]/dt = 0$, substitution of the value derived for $[Cl_2]$ from eq 9 into eq 8 yields eq 10. If $k_3[PAH]$

$$\frac{-d[PAH]}{dt} = \frac{k_1k_3\gamma^2[H^+][Cl^-][HOCl][PAH]}{k_2 + k_3[PAH]} \quad (10)$$

$$\frac{-d[PAH]}{dt} = \frac{k_3\gamma^2[H^+][Cl^-][HOCl]}{K_{Cl_2}}[PAH] \quad (11)$$

$\ll k_2$ (11 s^{-1} (*35*)), then eq 10 reduces to eq 11, which is consistent with what was observed. Indeed, this latter

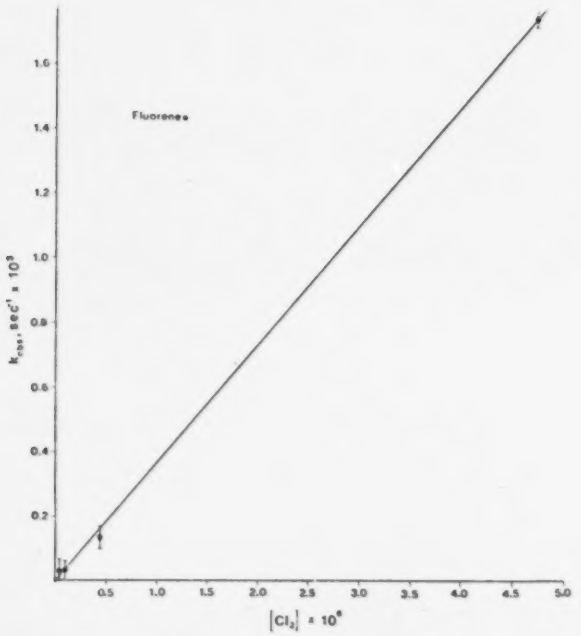


Figure 3. Dependence of k_{obsd} upon $[Cl_2]$ at low pH for fluorene.

assumption appears to be valid since the calculated value of $k_3[PAH]$ is $\sim 0.006\ s^{-1}$ or less at the PAH concentration employed.

The major products observed at low pH were phenanthrene-9,10-dione, 9-chlorophenanthrene, 2-chlorofluorene, and 3-chlorofluoranthene (Tables I–IV).

High pH. For phenanthrene reactions in which hypochlorite made up 95% or more of the total chlorine concentration (pH >8.8), the pseudo-first-order rate constants observed (k_{obsd}) were found to be closely approximated by $k_{obsd}^{OCl^-}$ (eq 12). Thus, nonlinear regression analysis of

$$k_{obsd}^{OCl^-} = [OCl^-]/(A + B[OCl^-]) \quad (12)$$

the experimental data provided values for the parameters A and B of $(3.17 \pm 0.24) \times 10^{-2}$ M s and $(5.86 \pm 0.12) \times 10^2$ s, respectively. The major products were phenanthrene 9,10-oxide, phenanthrene-9,10-dione, and 9,10-dihydrophenanthrenediol.

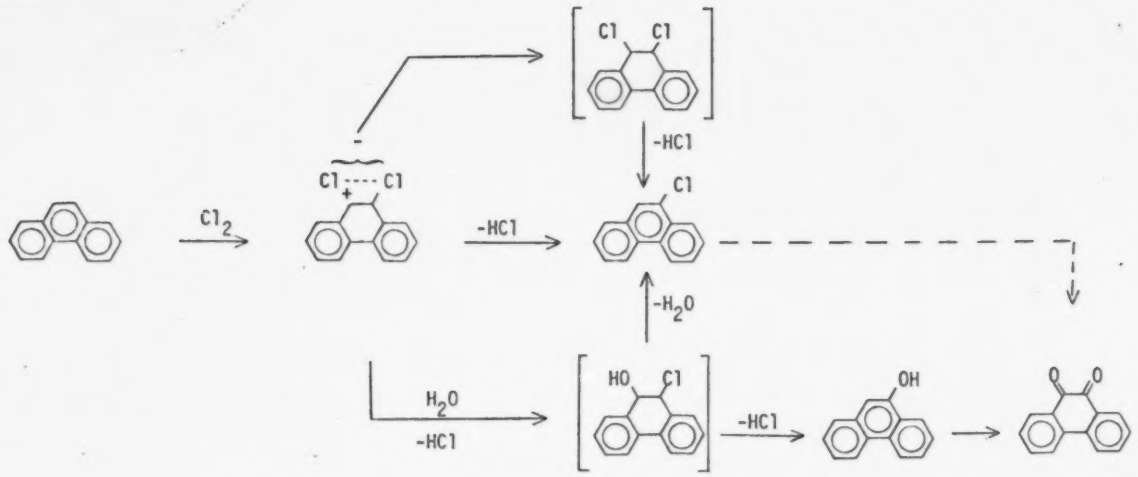
Intermediate pH. Hypochlorous acid is the predominant chlorine species present in the pH range 5–7.5. The product distributions obtained for phenanthrene were similar to those obtained in the pH range where hypochlorite predominated (Table I).

Correlation of All Rate Data. Equation 13 was found

$$k_{obsd}^{all} = \frac{C[HOCl] + [OCl^-]}{A + B[OCl^-] + D[HOCl] + E[Cl_2]} + k_3[Cl_2] \quad (13)$$

to provide a reasonable fit for the phenanthrene data obtained over the entire pH range. Thus, nonlinear regression analysis of the observed k_{obsd} values utilizing eq 13, in which k_{obsd}^{all} is the predicted value of k_{obsd} and k_3, A, and B were fixed at the values derived above, gave values for C, D, and E of 8.50 ± 3.31, $(1.78 \pm 1.02) \times 10^3$ s, and $(2.19 \pm 0.95) \times 10^9$ s, respectively.

A plot of the predicted k_{obsd} values, k_{obsd}^{all}, vs. pH for several total chlorine concentrations is shown in Figure 4. The general profile of the individual curves is quite similar to that obtained in the previously mentioned study of pyrene and benzo[*ghi*]perylene (*7*). Furthermore, at pH



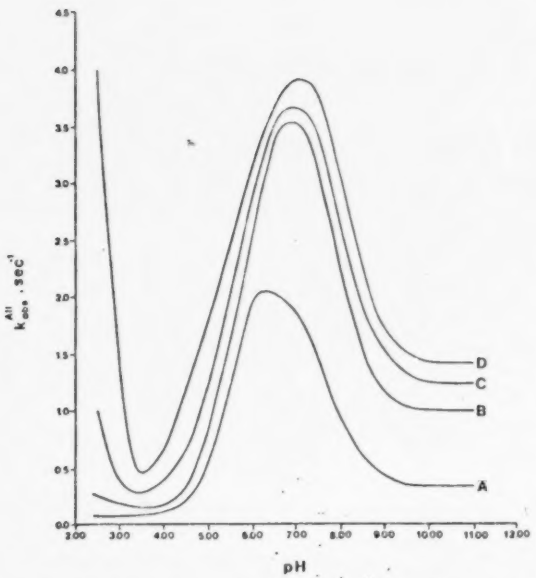


Figure 4. Calculated reaction rate profiles for phenanthrene (eq 13): [total chlorine] = [chloride] = 1.41×10^{-5} (A), 7.0×10^{-5} (B), 1.4×10^{-3} (C), 2.8×10^{-4} (D). Experimental and calculated data for phenanthrene kinetics are available as supplemental material.

6.8 the k_{obsd} values for these compounds calculated from the data in this study (7) were identical with the corresponding k_{obsd}^{all} value for phenanthrene in the present study (3.6×10^{-3} s^{-1}).

The rate of reaction of phenanthrene in aqueous solutions is therefore at least approximated, if not described, by eq 14. Examination of eq 1 and 2 and Figure 4 provides

$$\frac{-d[PAH]}{dt} = \frac{[OCl^-][PAH]}{A + B[OCl^-] + D[HOCl] + E[Cl_2]} + \frac{C[HOCl][PAH]}{A + B[OCl^-] + D[HOCl] + E[Cl_2]} + k_3[Cl_2][PAH] \quad (14)$$

some insight into the relative contributions of each of the three terms in eq 14 to the observed rate. At pH $\gtrsim$8.7 only the [OCl$^-$] term (first term) is significant. Between pH $\sim$8.7 and 7.5 the [OCl$^-$] terms becomes less important while the [HOCl] term (second term) becomes predominant. Between pH 7.5 and 4 the [HOCl] term remains the only significant term and the [Cl$_2$] term (third term) is significant at a pH below $\sim$4.

Scheme II

$$HOCl \xrightarrow{k_1'} I$$

$$OCl^- \xrightarrow{k_2'} I$$

$$HOCl + I \xrightarrow{k_3'} \text{unreactive species}$$

$$OCl^- + I \xrightarrow{k_4'} \text{unreactive species}$$

$$Cl_2 + I \xrightarrow{k_5'} \text{unreactive species}$$

$$PAH + I \xrightarrow{k_6'} \text{products}$$

$$I \xrightarrow{k_7'} \text{unreactive species}$$

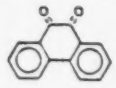
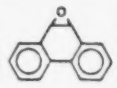
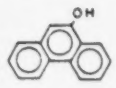
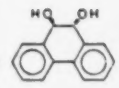
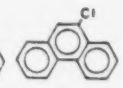
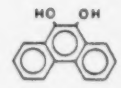
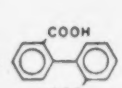
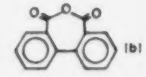
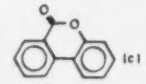
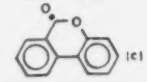
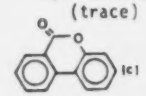
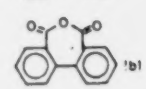
Possible routes to the various phenanthrene products formed at low pH are illustrated in Scheme I. This sequence is consistent with the observed kinetic expression (eq 8) and with a reported study of phenanthrene in acetic acid (*36*).

The picture at higher pH levels is considerably more complex. A key feature of the experimental data (expressed by eq 14 and Figure 4) is the relative insensitivity of the reaction rate at pH >3.5 to increased total chlorine concentration. An interpretation of this feature is that an intermediate is formed that can react with the PAH as well as with the Cl$_2$, HOCl, and OCl$^-$. The products of the latter (non-PAH) reactions could be species that are unreactive toward the PAH. The reactive intermediate could also decompose to an unreactive species. An outline of this interpretation is provided in Scheme II.

If a steady state is assumed for the intermediate (i.e., d[I]/dt = 0), then the rate equation consistent with this model is given by eq 15. If k_6'[PAH] is much less than

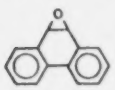
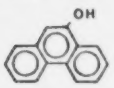
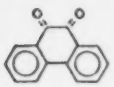
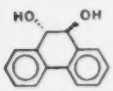
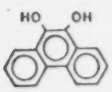
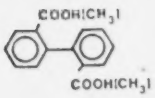
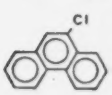
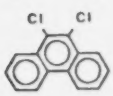
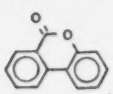
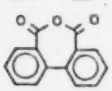
$$\frac{-d[PAH]}{dt} = \frac{k_1'k_6'[HOCl] + k_2'k_6'[OCl^-]}{k_3'[HOCl] + k_4'[OCl^-] + k_5'[Cl_2] + k_6'[PAH] + k_7'} \times (PAH) \quad (15)$$

Table I. Dependence of Phenanthrene Product Distribution upon Chlorine Species[a]

pH	[HOCl]	[OCl⁻]	[Cl_2]								Other	Reaction Period (Minutes)	X·$t_{\frac{1}{2}}$
10.06	8.69×10^{-7}	2.90×10^{-4}	0	3%	57%		present					44.1	4
8.86	2.43×10^{-6}	5.10×10^{-5}	0	1	45		20					67.7	4
8	2.8×10^{-4}	7.8×10^{-4}	0	present[b]			present[b]		present[c]	present[b,d]	traces	2580	5
7.70	1.57×10^{-4}	2.28×10^{-4}	0	2	87		4					141	5.5
6.84	1.41×10^{-4}	2.82×10^{-5}	6.00×10^{-12}	20	13	2	51	trace				3942	7
6	5.8×10^{-4}	1.7×10^{-5}	9.2×10^{-10}	present[b]	e	present[b]		trace[b]	present[c]			1380	4
													
6	7.3×10^{-4}	2.1×10^{-5}	1.5×10^{-9}	present[b]	e		present[b]	present[b]	present[b]			1063	5
5.70	4.99×10^{-5}	7.26×10^{-7}	4.17×10^{-11}	22	~66	present	present					1629	4
5.00	3.40×10^{-4}	9.88×10^{-7}	3.22×10^{-9}	62		trace	35					1629	4
4.04	2.72×10^{-4}	8.67×10^{-8}	2.21×10^{-8}	49		trace	36					402	5
3.03	4.45×10^{-3}	1.39×10^{-8}	5.43×10^{-7}	32		19	34				9,10-dichloro (7%)	32	5
3.03	6.54×10^{-5}	2.04×10^{-9}	1.15×10^{-8}	48		trace	37				9,10-dichloro (trace)	419	3.5
3	6.5×10^{-4}	1.9×10^{-8}	1.9×10^{-5}	present[b]			present[b]					117	5
													

[a] Percent yield based on HPLC data with respect to authentic standard. [b] Mass spectra and GC retention time identical with those of an authentic standard. [c] Tentative assignment based on GC-MS data. [d] Derivatized with diazomethane prior to GC-MS analysis. [e] Epoxide originally present presumably rearranged and hydrolyzed.

Table II. Chromatographic and Mass Spectral Data for Phenanthrene Products

compound	rel retention time (HPLC)[a]	rel retention time (GC)[a]	mass spectrum
	0.816	1.12	194 ($M^{+\cdot}$, 64), 178 (18), 166 (52), 165 (100), 163 (18), 139 (12)
	0.816	1.23	194 ($M^{+\cdot}$, 71), 166 (53), 165 (100), 163 (14), 139 (18)
	0.726	1.29	208 ($M^{+\cdot}$, 14), 180 (100), 152 (57), 151 (29), 150 (20)
	0.614	1.24	212 ($M^{+\cdot}$, 20), 194 (22), 181 (62), 166 (66), 165 (100), 163 (11), 152 (25)
		1.08	210 ($M^{+\cdot}$, 2), 181 (100), 153 (15), 152 (39)
		1.10	270 ($M^{+\cdot}$, 4), 239 (4), 211 (100), 180 (8)
	1.128	1.14	212 ($M^{+\cdot}$, 93), 214 (33), 177 (36), 176 (62), 174 (15), 88 (100), 75 (60)
	1.251	1.27	246 ($M^{+\cdot}$, 100), 248 (72), 212 (7), 211 (12), 210 (16), 177 (15), 176 (92), 175 (40), 174 (34)
 b		1.15	196 ($M^{+\cdot}$, 63), 168 (54), 139 (100), 114 (16), 113 (16)
		1.20	224 ($M^{+\cdot}$, 33), 180 (100), 152 (77), 151 (34), 150 (19), 126 (15), 76 (39)

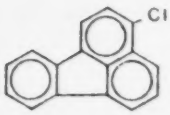
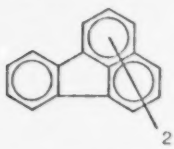
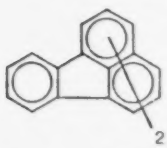
[a] Relative to phenanthrene. [b] Tentative assignment based on mass spectrum.

($k_3'[HOCl] + k_4'[OCl^-] + k_5'[Cl_2] + k_7'$), then eq 15 reduces to eq 16, which is consistent with the experimental data for reactions at pH ≳4 (eq 14.)

$$\frac{-d[PAH]}{dt} = \frac{\frac{k_1'}{k_2'}[HOCl] + [OCl^-]}{\frac{k_3'}{k_2'k_6'}[HOCl] + \frac{k_4'}{k_2'k_6'}[OCl^-] + \frac{k_5'}{k_2'k_6'}[Cl_2] + \frac{k_7'}{k_2'k_6'}} \times [PAH] \quad (16)$$

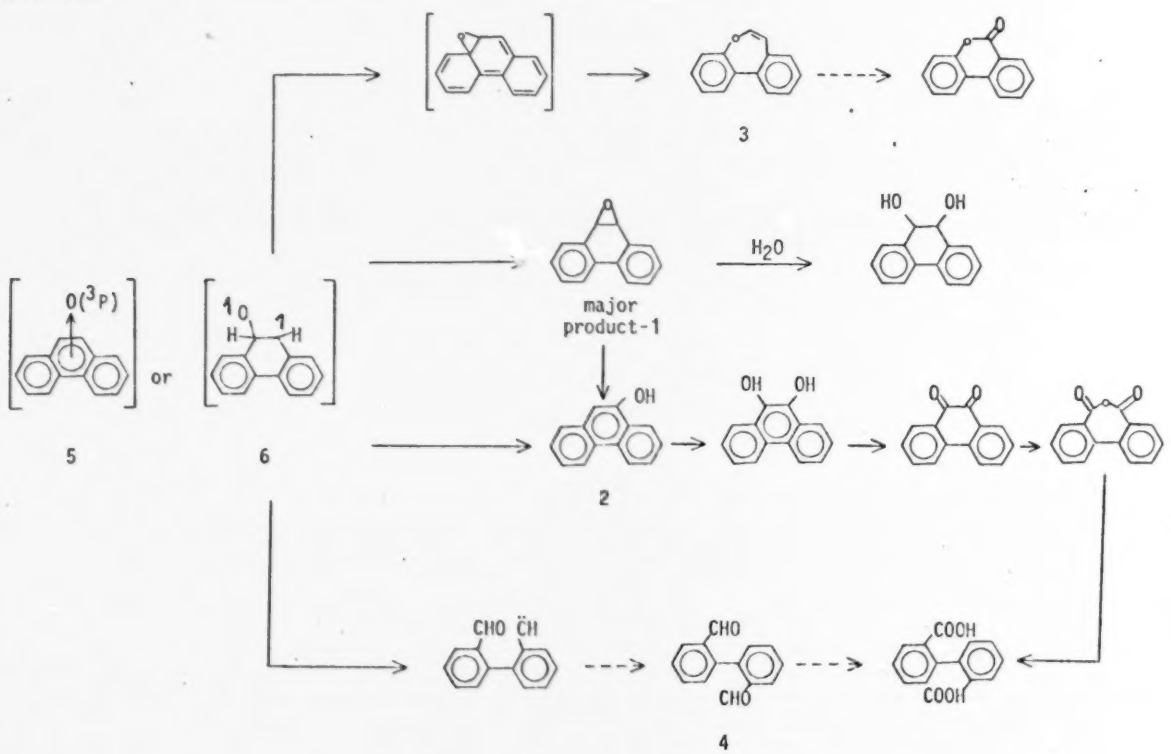
Several possibilities for the intermediate in this model were removed from serious consideration by experimentation. For example, although it has been suggested (*15*, *16*) that hydrogen peroxide may be an intermediate in the decomposition of hypochlorous acid, this species cannot logically represent the intermediate in this situation because of its observed low reactivity with phenanthrene (6×10^{-5} M H_2O_2, pH 7.1, $t_{1/2} > 24$ h; compare 2.6×10^{-5} M chlorine pH 7.1, $t_{1/2} \sim 5$ min). Furthermore, reactive species such as singlet oxygen molecules or $ClOO^-$, which may be produced by reaction of chlorine species with hydrogen peroxide (*37*, *38*), are apparently not involved since the addition of hydrogen peroxide to a phenanthrene solution containing chlorine did not accelerate the reaction rate.

Ground-state oxygen atoms represent an attractive possibility for the intermediate in this model (Scheme II), which is consistent with the isolated products derived from hydrolysis, rearrangement, and subsequent oxidation of the arene oxides or from the *o,o'*-dialdehyde (4, Scheme III, Table I (*28*, *33*)). $O(^3P)$ has been shown to be formed in hypochlorite solutions (*24*) and to be reactive toward the PAH (*39*). $O(^3P)$ is known (*24*) to react with hypochlorite to form chlorite and oxygen which have been shown in our investigation to be inactive toward the PAH (Scheme IV). Addition of chlorite (8×10^{-4} M), which is also known to react with $O(^3P)$ (*24*), dramatically retarded a phenanthrene reaction with chlorine (4×10^{-4} M) at pH 7.7. An analysis of the reaction mixtures for chlorite in the absence of *added* chlorite was not performed. Irradiation (350 nm) of another phenanthrene reaction with

compound	rel retention time (HPLC)[a]	rel retention time (GC)[a]	mass spectrum
	1.14	1.11	236 (100), 238 (30), 201 (24), 200 (31)
		1.22	270 (100), 272 (69), 235 (11), 237 (3), 200 (37), 199 (26), 198 (18)
		1.24	270 (100), 272 (69), 235 (12), 237 (3), 200 (40), 198 (19)

[a] Relative to fluoranthene.

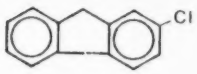
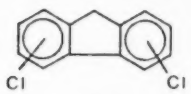
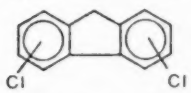
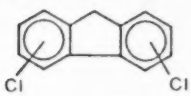
Scheme III



$$\frac{-d[PAH]}{dt} = \left[\frac{\frac{k_1''}{k_2''}[HOCl] + [OCl^-]}{\frac{k_6'' + k_7''}{k_2'' k_7''} + \frac{k_3''}{k_2'' k_7''}[HOCl] + \frac{k_4''}{k_2'' k_7''}[OCl^-] + \frac{k_5''}{k_2'' k_7''}[Cl_2]} \right] [PAH] \quad (17)$$

chlorine (1×10^{-5} M) at pH 7.7, which should increase the concentration of $O(^3P)$ (*24*), resulted in an accelerated rate of epoxide formation. Finally, the observed product distributions (Table I) are consistent with those that might be predicted on the basis of a literature report (*39*) of $O(^3P)$ reaction with phenanthrene in liquid carbon dioxide (Scheme III). In this latter study (*39*), the epoxide **1** and phenol **2** were the major products along with the oxepin **3** and the dialdehyde **4**. Possible pathways from these compounds to the minor products observed in the present study are shown in Scheme III. The untenable portion of this otherwise attractive mechanistic interpretation is the

Table IV. Chromatographic and Mass Spectral Data for Fluorene Products

compound	rel retention time (HPLC)[a]	rel retention time (GC)[a]	mass spectrum
	1.10	1.29	200 (19), 202 (7), 165 (100), 163 (22)
	1.18	1.54	234 (35), 236 (23), 201 (34), 199 (100), 164 (20), 163 (39)
	1.18	1.56	234 (36), 236 (25), 201 (34), 200 (25), 199 (100), 164 (21), 163 (41)
	1.18	1.61	234 (35), 236 (24), 201 (35), 199 (100), 164 (16), 163 (29)

[a] Relative to fluorene.

Scheme IV

$$HOCl + PAH \xrightarrow{k_1''} \text{complex (or intermediate)}$$

$$OCl^- + PAH \xrightarrow{k_2''} \text{complex (or intermediate)}$$

$$\text{complex + HOCl (or intermediate)} \xrightarrow{k_3''} PAH + \text{unreactive species } (ClO_2^- + O_2?)$$

$$\text{complex + } OCl^- \text{ (or intermediate)} \xrightarrow{k_4''} PAH + \text{unreactive species } (ClO_2^- + O_2?)$$

$$\text{complex + } Cl_2 \text{ (or intermediate)} \xrightarrow{k_5''} PAH + \text{unreactive species } (Cl_2O \rightarrow 2\ HOCl\ ?)$$

$$\text{complex (or intermediate)} \xrightarrow{k_6''} PAH + \text{unreactive species } [O(^3P)? \xrightarrow{OCl^-} ClO_2^-?]$$

$$\text{complex (or intermediate)} \xrightarrow{k_7''} PAH \text{ products}$$

direct formation of ground-state oxygen atoms from OCl^- or HOCl in the absence of ultraviolet radiation (*24*).

A more reasonable process is the formation of a complex (or intermediate) of HOCl or ^-OCl with the PAH, which may proceed to product or revert to the parent PAH (Scheme IV). The corresponding rate equation (eq 17) is consistent with the present experimental data, and complexes (5) or intermediate species (6) of this type have also been postulated in a number of studies of $O(^3P)$ reactions with aromatic systems (*39–42*). In addition, the kinetic expression suggests that the complex is nucleophilic and that the addition of electrophiles might retard the reaction (*43*).

Although the mechanism proposed above is in agreement with the observed rate data, it should be noted that an apparent induction period or a rate inhibition in mid-reaction course was occasionally observed at higher pH. We have ascribed this phenomenon to nucleation (or surface adsorption) of the PAH, and precautions such as submicron filtration of the solutions were found to minimize these occurrences. However, on the basis of these observations an appropriate final caveat is the recognition of the possible involvement of some type of radical process at higher pH values.

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Supplementary Material Available

Experimental and calculated data for phenanthrene and fluoranthene kinetics (8 pages) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper or microfiche (105 × 148 mm, 24× reduction, negatives) may be obtained from Distribution Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, DC 20036. Full bibliographic citation (journal, title of article, author, page number) and prepayment, check or money order for $13.50 for photocopy ($15.50 foreign) or $6.00 for microfiche ($7.00 foreign), are required.

Registry No. Phenanthrene, 85-01-8; fluorene, 86-73-7; fluoranthene, 206-44-0; chlorine, 7782-50-5; 9,10-dichlorophenanthrene, 17219-94-2.

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